Catalysis of Arene Hydrogenation by Thermally Activated Silica

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INTRODUCTION

Silica has been used as a support material for a variety of catalysts, usually noble metals or transition metal oxides, for many years. Recent articles attest to its continued popularity.[1] For the most part, discussions of catalytic mechanisms have focussed on the metals and ignored the support.[2] Its role in these catalytic processes has usually been considered to be passive. It is often coated with various organic compounds for use as a chromatographic stationary phase, but even when the organic ligand is attached chemically, the silica itself is regarded essentially as an anchor.[3] This has also been true for studies of thermolysis mechanisms where it was desired to immobilize organic substrates for comparison with naturally occurring nonvolatile materials such as coal.[4] Studies in which silica-immobilized substrates have been heated under pressure of H_2 and D_2 have shown no special effects that might be attributed to catalytic involvement of the support.[5]

However, recent work by Bittner, Bockrath and Solar[6] showed that fumed silica, after thermal activation above 330 °C under argon flow, will catalyze the reaction, $H_2 + D_2 \rightarrow 2$ HD, at temperatures as low as 120 °C in a pulse-flow microreactor and will also catalyze the hydrogenation of ethene to ethane at 150 °C, producing ethane-d_6 when D_2 is used as a flow gas. This suggested that silica, by itself, could serve as a catalyst for hydrogenation reactions. Accordingly, we studied the reaction of thermally-activated, fumed silica and H_2 with selected alkenes in a static reactor and showed that it could function as a hydrogenation catalyst,[7] allowing stilbene and other alkenes to be hydrogenated at temperatures at least 100 °C below those required for a purely thermal reaction. As part of that study, we also showed that hydrogenation of diphenylacetylene gave predominantly the thermodynamically less stable *cis* isomer of stilbene, demonstrating *syn* hydrogenation in a manner reminiscent of that observed with metal catalysts.[8]

We also reported our preliminary observation that under some circumstances aromatic ring reduction was catalyzed by thermally-activated, fumed silica, but noted that this behavior varied with the source of the particular fumed silica employed. We now wish to report experiments intended to probe this phenomenon and to offer possible explanations.

EXPERIMENTAL

Materials. Hydrogenation substrates were the best available commercial grade. Fumed silica was obtained both from Cabot Corporation (Cab-O-Sil grade M-5) or from Aldrich Chemical Co. (both 0.014 and 0.007 micron size were employed.) Several different lot numbers of Cabot silica were tried some were activatable for carrying out aromatic hydrogenations, others were not. The Aldrich silicas proved inactive unless treated with HCl as described below. Tetramethyl orthosilicate was purchased from Aldrich Chemical Co. It produced an activatable silica after hydrolysis as described below.

HCl Treatment of Fumed Silica. Approximately 800 to 900 mg of commercial fumed silica was allowed to stir for approximately 15 min in 50 mL of concentrated HCl. The resulting slurry was then separated by vacuum filtration through a 50 M fritted glass filter. This produced a dull white filter cake which was allowed to dry by passing a stream of air over the cake for roughly two hours, breaking the caked silica periodically with a glass rod. The cake was allowed to dry to a point where it could be transferred conveniently, usually weighing approximately 2 g at this point. This damp silica (ca. 1 g) was then transferred into the glass reactor tube, initially open at both ends. It was activated by passing argon over the material at 430 °C for 10 to 16 h. Following the thermal activation, the non-capillary end of the reactor was sealed. Solid substrates were introduced through the wide opening in the reaction tube before sealing. Liquid substrates were introduced by syringe after sealing.

Preparation of Silica by Hydrolysis of Tetramethyl Orthosilicate. Tetramethyl orthosilicate (2 mL) was added to approximately 50 mL of deionized water. The mixture was allowed to stand at approximately 25 °C for 10 to 16 h. The resultant brittle cake was broken up with a glass stirring rod and dried in a stream of air as described for hydrolyzed fumed silica. This produced approximately 1 g of silica which was reduced to 800 mg after activation. In some experiments, the tetramethyl orthosilicate was treated with aqueous HCl prepared by passing gaseous HCl into deionized water. Treatment with aqueous HCl produced a solid gel immediately.

Hydrogenation Procedure. Reactions were carried out in glass bulbs of approximately 12 mL volume with a 16 cm section of 1 - 2 mm capillary attached to one end. The procedures for activating the catalyst, loading the reactors and carrying out the reactions have been described in earlier publications.[7]

Workup Procedures. In some cases, reaction vessels were cracked open and the silica hydrolyzed as described earlier. In others, products were removed by distillation at pressures of less than 0.1 Torr into a liquid nitrogen-cooled trap. Reaction products were combined with a measured volume of standardized biphenyl or naphthalene solution in CH_2Cl_2 then analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS). Recoveries were generally greater than 90 % based on response factors estimated from carbon numbers or standard mixtures when available.

RESULTS AND DISCUSSION

In our previous papers[7] we reported that fumed silica which was activated by heating under argon flow at 350 °C promoted the hydrogenation of diphenylethane (DPE) to a mixture of cyclohexylphenylethane (CPE) and dicyclohexylethane (DCE). When the reaction was carried out using D_2 the products were highly deuterated, with the CPE showing ions of mass d_6 to d_{18} with maximum intensity at d_{11} and the DCE showing ions of mass d_{12} to d_{26} with maximum intensity at d_{19} . Using the same silica samples, naphthalene was hydrogenated to less than 2% conversion. Moreover, inclusion of naphthalene along with DPE prevented hydrogenation of DPE. During the course of these experiments, we exhausted our bottle of fumed silica and found that a new sample, obtained from the same supplier, but displaying a different lot number, used in the same procedure, failed to promote hydrogenation of DPE. Subsequent experiments showed that some fumed silica samples worked and some did not. Samples obtained from a second supplier in two different particle sizes also failed to promote the reaction. For reasons which may or may not explain the effect of the procedure, we tried treating the ineffective samples with concentrated HCl prior to thermal activation. This procedure had the desired effect in that the resultant samples promoted hydrogenation of DPE.

We then determined the effect of the various silicas on the reaction of H_2 with diphenylmethane. The products of this reaction are shown in Figure I and yields are listed in Table I. It will be noted that the variability observed for DPE with different silica sources is also observed with DPM. In an attempt to rule out trace metal contamination as a source of the differing catalytic activities, some of the silicas were subjected to ICP (inductively coupled plasm) analysis. The results are listed in Table II. We would suggest that the values determined, which generally border on the limits of experimental detection, are not sufficiently different for these samples to explain their differing effectiveness in promoting the hydrogenation of DPM. Data for the two ineffective silicas (C2 and A1) do not differ in any systematic way from the data for C1 and C3.

In the absence of a catalytic contaminant, we must tentatively conclude that structural differences within the silica matrix are responsible for differing catalytic effectiveness. As in the DPE reaction, treatment of inactivatable silica with concentrated HCl prior to the thermal activation process has the effect of producing an activatable catalyst (compare entries 5 and 6 in Table I). No chlorinated products were detected when HCl-treated silica was used for hydrogenations and it is therefore hypothesized that the effect of the HCl treatment is to disrupt the silica matrix such that subsequent thermal dehydration can produce sites which are catalytic for the hydrogenation. Thermal dehydration of fumed silica has been recently studied by NMR which showed that hydrogen bonded surface silanols are gradually reduced in number.[9] In our case, it is suspected that the disruption and dehydration is promoted by HCl during the thermal activation stage rather than during the HCl treatment itself because thorough water washing of the HCl-treated material prior to heating precludes activation as shown by entry 7 in Table I.

To provide further evidence that silica itself is responsible for promotion of arene hydrogenation, silica samples were prepared by hydrolysis of tetramethyl orthosilicate $(Si(OCH_3)_4)$ using deionized water alone and with deionized water containing HCl (see Experimental). Both treatments produced thermally activatable silicas as shown by entries 8 and 9 in Table I. Having established that treatment of 0.014 micron fumed silica with aqueous HCl followed by thermal

Table I. Yields of Products from Treatment of Diphenylmethane **DPM** with H_2 (14 MPa) in the Presence of Various Thermally-Activated Fumed Silicas.

Silica Type	Products (%)				
	CPM	**DCM**	**PhMe**	**CMe**	**PhH**
C1[a]	39	12	n.d.[f]	n.d.[f]	n.d.[f]
C2[a]	3	0.3	n.d.[f]	n.d.[f]	n.d.[f]
C3[a]	31	11	0.24	<0.1	0.24
A1[b]	1.1	0.2	0.15	0.14	0.14
A2[b]	2.7	0.4	0.16	<0.1	0.16
A2 (HCl)[c]	25	54	0.2	0.2	0.4
A2 (HCl/H_2O)[d]	4.7	<0.1	0.3	<0.1	0.1
TMS (H_2O)[e]	12	62	0.25	0.6	0.7
TMS (HCl)[e]	28	60	0.3	1.0	1.0

Notes for Table I: [a] C1, C2 and C3 are Cabot Grade M5 (0.014 micron) fumed silicas having different lot numbers. [b] A1 is Aldrich 0.007 micron fumed silica; A2 is Aldrich 0.014 micron fumed silica. [c] A2 (HCl) is Aldrich 0.014 micron fumed silica treated with concentrated HCl as described in the experimental section. [d] A2 (HCl/H_2O) is the same as A2 (HCl) except for being washed with water to neutral pH before thermal activation. [e] TMS (H_2O) is silica produced by hydrolysis of tetramethyl orthosilicate with deionized water. TMS (HCl) is the same with HCl added. [f] Not determined.

Table II. Trace Metal Content of Silicas used for the Hydrogenation of **DPM** in Table I.

Silica Type[a]	Metal Content (ppm)						
	Ca	Cr	Co	Cu	Fe	Mn	Ni
C1	<30	5	<4	16	30	<2	15
C2	200	3	<4	28	68	<2	38
C3	60	<2	<4	20	67	<2	15
A1	<30	<2	6	20	40	<2	<3

[a] See notes for Table I.

activation produces an active catalyst for the hydrogenation of **DPE** and **DPM**, we reexamined the reaction of naphthalene. Results for this and other substrates are shown in Figure II. As before, only a small conversion (4%) to tetralin could be accomplished either with A2 (HCl) or withTMS (H_2O). Biphenyl was also resistant but toluene showed substantial reaction. Chloronaphthalene gave a 22% yield of naphthalene with silica A2 under the same conditions.

CONCLUSIONS

The pattern which is emerging from these studies shows that when silica possesses the proper structural characteristics, the nature of which are unknown at the present time, it can then be converted by heating at 350 °C to a form which will catalyze the hydrogenation of certain arenes. Some commercial fumed silicas work, others do not. Those that do not work benefit from treatment with aqueous HCl prior to thermal activation. One commercial sample which was ineffective in the **DPM** reaction also refused activation to promote the $H_2 + D_2 \rightarrow$ HD reaction in a pulsed microreactor. HCl treatment remedied this situation. Silica prepared from hydrolysis of Si(OMe)$_4$ with pure water proved an effective catalyst after heating. We have found that arenes which are most extensively hydrogenated are those with benzylic C-H groups, **DPE**, **DPM**, or **PhMe**. Naphthalene, which should be easier to hydrogenate in the thermodynamic sense, gave only a few percent conversion under the same conditions and seemed to poison the surface toward reactions with arenes which could be hydrogenated in its absence. As a working hypothesis, we suggest that silicas with appropriate structural features, promote isomerization of alkyl arenes to cyclic polyenes

which are then rapidly reduced. This scheme is shown in Figure I. With **DPM**, a small but significant amount of hydrocracking is also observed. We suggest that this is a high-temperature, alternate route for partially hydrogenated intermediates as shown in Figure I. Preliminary results indicate that hydrocracking is the major reaction outcome when **DPM** is treated with H_2 and silica at 450 °C.

ACKNOWLEDGMENTS

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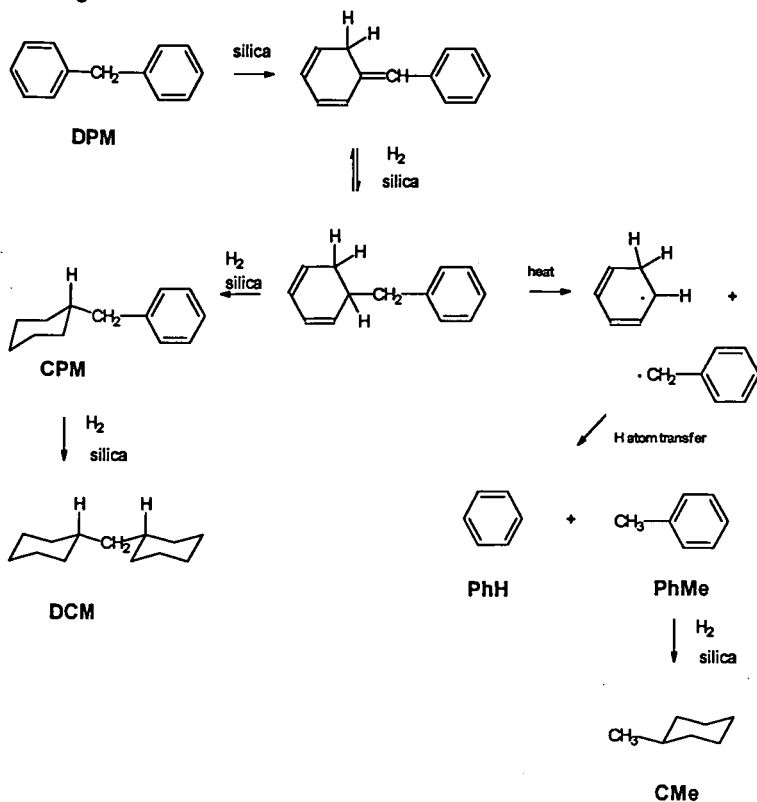
Figure I

DPM

silica →

↕ H$_2$ / silica

H$_2$ / silica ←

CPM

↓ H$_2$ / silica

DCM

heat →

· CH$_2$—Ph

↙ H atom transfer

PhH + CH$_3$— **PhMe**

↓ H$_2$ / silica

CH$_3$— **CMe**

Figure II

CH$_3$ → silica A2 → H / CH$_3$

33%

silica A2 or TMS (H$_2$O) →

4%

silica TMS (H$_2$O) →

1.7%

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